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SURFACE-TREATED SUPERABSORBENT POLYMER PARTICLES

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Surface-treated superabsorbent polymer particles obtained by mixing 100 parts by weight of superabsorbent polymer particles with 0.001 to 10 parts by weight of a hydroxyalkylurea, and heating the surface-treated superabsorbent polymer particles to crosslink molecular chains existing at least in the vicinity of the surfaces of the superabsorbent polymer particles is disclosed. Surface crosslinking the superabsorbent polymer particles with a hydroxyalkylurea substantially increases both the rate of liquid absorption and the quantity of liquid absorbed and retained by the superabsorbent particles. Data supplied from the esp@cenet database - Worldwide

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**WO 01/89591 A2**

(54) Title: SURFACE-TREATED SUPERABSORBENT POLYMER PARTICLES

(57) Abstract: Surface-treated superabsorbent polymer particles obtained by mixing 100 parts by weight of superabsorbent polymer particles with 0.001 to 10 parts by weight of a hydroxyalkylurea, and heating the surface-treated superabsorbent polymer particles to crosslink molecular chains existing at least in the vicinity of the surfaces of the superabsorbent polymer particles is disclosed. Surface crosslinking the superabsorbent polymer particles with a hydroxyalkylurea substantially increases both the rate of liquid absorption and the quantity of liquid absorbed and retained by the superabsorbent particles.

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**SURFACE-TREATED SUPERABSORBENT  
POLYMER PARTICLES**

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**FIELD OF THE INVENTION**

The present invention relates to surface-crosslinked superabsorbent polymer particles, and to methods of producing the surface-crosslinked superabsorbent particles. The present invention also relates to the use of the surface-crosslinked particles in articles, such as diapers, catamenial devices, and wound dressings. More particularly, the present invention relates to surface treating superabsorbent polymer (SAP) particles, such as a neutralized, crosslinked, homopolymer or copolymer of acrylic acid, with a hydroxyalkylurea to substantially improve the water absorption and water retention properties of the SAP particles.

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**BACKGROUND OF THE INVENTION**

Water-absorbing resins are widely used in sanitary goods, hygienic goods, wiping cloths, water-retaining agents, dehydrating agents, sludge coagulants, disposable towels and bath mats, disposable door mats, thickening agents, disposable litter mats for pets, condensation-preventing agents, and release control agents for various chemicals.

Water-absorbing resins are available in a variety of chemical forms, including substituted and unsubstituted natural and synthetic polymers, such as hydrolysis products of starch acrylonitrile graft polymers, carboxymethylcellulose, crosslinked poly-

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acrylates, sulfonated polystyrenes, hydrolyzed polyacrylamides, polyvinyl alcohols, polyethylene oxides, polyvinylpyrrolidones, and polyacrylonitriles.

Such water-absorbing resins are termed  
5 "superabsorbent polymers," or SAPs, and typically are lightly crosslinked hydrophilic polymers. SAPs are generally discussed in Goldman et al. U.S. Patent Nos. 5,669,894 and 5,559,335, the disclosures of which are incorporated herein by reference. SAPs  
10 can differ in their chemical identity, but all SAPs are capable of absorbing and retaining amounts of aqueous fluids equivalent to many times their own weight, even under moderate pressure. For example, SAPs can absorb one hundred times their own weight,  
15 or more, of distilled water. The ability to absorb aqueous fluids under a confining pressure is an important requirements for an SAP used in a hygienic article, such as a diaper.

As used here and hereafter, the term "SAP  
20 particles" refers to superabsorbent polymer particles in the dry state, i.e., particles containing from no water up to an amount of water less than the weight of the particles. The term "particles" refers to granules, fibers, flakes, spheres, powders,  
25 platelets, and other shapes and forms known to persons skilled in the art of superabsorbent polymers. The terms "SAP gel" and "SAP hydrogel" refer to a superabsorbent polymer in the hydrated state, i.e., particles that have absorbed at least their weight  
30 in water, and typically several times their weight in water. The terms "surface-treated SAP particle" and "surface-crosslinked SAP particle" refer to an SAP particle having its molecular chains present in

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the vicinity of the particle surface crosslinked by a compound applied to the surface of the particle. The term "surface crosslinking" means that the level of functional crosslinks in the SAP particle in the vicinity of the surface of the particle is generally higher than the level of functional crosslinks in the SAP particle in the interior of the particle.

SAP particles can differ in ease and cost of manufacture, chemical identity, physical properties, rate of water absorption, and degree of water absorption and retention, thus making the ideal water-absorbent resin a difficult composition to design. For example, the hydrolysis products of starch-acrylonitrile graft polymers have a comparatively high ability to absorb water, but require a cumbersome process for production and have the disadvantages of low heat resistance and decay or decomposition due to the presence of starch. Conversely, other water-absorbent polymers are easily and cheaply manufactured and are not subject to decomposition, but do not absorb liquids as well as the starch-acrylonitrile graft polymers.

Therefore, it would be extremely advantageous to provide a method of increasing the water absorption properties of a stable, easy to manufacture SAP particles to match the superior water absorption properties of a difficult to manufacture particle. Likewise, it would be advantageous to further increase the liquid absorption properties of already superior SAP particles.

In addition, conventional SAP particles all have a serious defect in that their rates of liquid absorption are lower than fluff pulp and

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paper. For example, when urine is excreted on a disposable diaper containing conventional SAP particles, the urine can remain in contact with the skin for a relatively long time and make the wearer uncomfortable. This is attributed to the low rate at which the diaper can absorb urine.

Attempts have been made to increase the liquid absorption rate by increasing the surface area of the SAP particle, i.e., by decreasing its particle size. However, when the particle size of the SAP particle is decreased, it generally forms a "fish eye" upon contact with urine, which retards the speed of liquid absorption. When the SAP particles are in the form of granules, each granule constitutes a "fish eye" and the speed of liquid absorption decreases. SAP particles in flake form exhibit a moderate increase in the speed of liquid absorption. But, SAP flakes are bulky and are difficult to transport and store.

Initially, the swelling capacity of an SAP particle on contact with liquids, also referred to as free swelling capacity, was the main factor in the design and development of SAP particles. Later, however, it was found that not only is the amount of absorbed liquid important, but the stability of the swollen gel, or gel strength, also important. The free swelling capacity, on one hand, and the gel strength, on the other hand, represent contrary properties. Accordingly, SAP particles having a particularly high absorbency typically exhibit a poor gel strength, such that the gel deforms under pressure (e.g., the load of a body), and prevents further liquid distribution and absorption.

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A balanced relation between absorptivity (gel volume) and gel strength is desired to provide proper liquid absorption, liquid transport, and dryness of the diaper and the skin when using SAP particles in a diaper. In this regard, not only is the ability of the SAP particle to retain a liquid under subsequent pressure an important property, but absorption of a liquid against a simultaneously acting pressure, i.e., during liquid absorption also is important. This is the case in practice when a child or adult sits or lies on a sanitary article, or when shear forces are acting on the sanitary article, e.g., leg movements. This absorption property is referred to as absorption under load.

Currently, there is a trend to reduce the size and thickness of sanitary articles for esthetic and environmental reasons (e.g., reduction of waste in landfills). This is accomplished by reducing the large volume of fluff pulp and paper in diapers, and increasing the amount of SAP particles. The SAP particles, therefore, have to perform additional functions with respect to liquid absorption and transport which previously were performed by the fluff pulp and paper, and which could not be accomplished satisfactorily with conventional SAP particles.

Investigators have researched various methods of improving the amount of liquid absorbed and retained by SAP particles, especially under load, and the rate at which the liquid is absorbed. One preferred method of improving the absorption and retention properties of SAP particles is to surface treat the SAP particles.

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The surface treatment of SAP particles is well known. For example, U.S. Patent No. 4,043,952 discloses the use of polyvalent metal compounds as surface treating compounds. U.S. Patent No.

5 4,051,086 discloses the use of glyoxal as a surface treatment to improve the absorption rate of SAP particles. The surface treatment of SAP particles with crosslinking agents having two or more functional groups capable of reacting with pendant  
10 carboxylate or other groups contained on the polymer comprising the SAP particle is disclosed in various patents. The surface treatment improves absorbency and gel rigidity to improve liquid flowability and prevent SAP particle agglomeration, as well as improving gel strength.  
15

As disclosed in the art, the SAP particles are either mixed with the surface-crosslinking agent optionally using small amounts of water and/or an organic solvent, or an SAP hydrogel containing 10%  
20 to 40%, by weight, water is dispersed in a hydrophilic or hydrophobic solvent and mixed with the surface-crosslinking agent.

Prior surface crosslinking agents include diglycidyl ethers, halo epoxy compounds, polyols,  
25 polyamines, polyisocyanates, polyfunctional aziridine compounds, and di- or tri-alkylhalides. Regardless of the identity of the surface crosslinking agent, the agent used for the surface treatment has at least two functional groups, and the SAP particles  
30 are heated after the surface crosslinking agent is applied to the surface of the SAP particles.

Surface-crosslinked SAP particles, in general, exhibit higher liquid absorption and reten-



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tion values than SAP particles having a comparable level of internal crosslinks, but lacking surface crosslinking. Internal crosslinks arise from polymerization of the monomers comprising the SAP particles, and are present in the polymer backbone. It has been theorized that surface crosslinking increases the resistance of SAP particles to deformation, thus reducing the degree of contact between surfaces of neighboring SAP particles when the resulting hydrogel is deformed under an external pressure. The degree to which absorption and retention values are enhanced by surface crosslinking is related to the relative amount and distribution of internal and surface crosslinks, and to the particular surface crosslinking agent and method of surface crosslinking.

As understood in the art, surface-cross-linked SAP particles have a higher level of crosslinking in the vicinity of the surface than in the interior. As used herein, "surface" describes the outer-facing boundaries of the particle. For porous SAP particles, exposed internal surface also are included in the definition of surface.

Prior methods of performing surface crosslinking of SAP particles are disclosed, for example, in Obayashi U.S. Patent No. 4,541,871, WO 92/16565, WO 93/05080, WO 99/42494, WO 99/43720, Alexander U.S. Patent No. 4,824,901, Johnson U.S. Patent No. 4,789,861, Makita U.S. Patent No. 4,587,308, Tsubakimoto U.S. Patent No. 4,734,478, Kimura et al. U.S. Patent No. 5,164,459, DE 4,020,780, and EPO 509,708. Surface crosslinking of SAPs is generally discussed in F.L. Buchholz et al., ed., "Modern

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Superabsorbent Polymer Technology," Wiley-VCH, New York, NY, pages 97-108 (1998).

5 A problem encountered in several prior compounds and methods used to surface crosslink SAP particles is the relatively high temperature re-  
quired to form the surface crosslinks between the SAP and the surface crosslinking agent. Typically, temperatures in excess of 180°C are required to form  
10 the surface crosslinks. At such temperatures, the SAP particle has a tendency to degrade in color from white or off-white to tan or brown. Such color degradation provides an SAP particle that is esthetically unacceptable to consumers. In addition, a high surface crosslinking temperature can  
15 increase the residual monomer content of the SAP particle, which can lead to adverse environmental and health effects, or can lead to rejection of the SAP particles for failing to meet specifications.

20 The present invention is directed to surface-treated SAP particles that overcome the disadvantages associated with prior surface crosslinking agents and with prior surface crosslinked SAP particles.

#### 25 SUMMARY OF THE INVENTION

30 The present invention is directed to surface-treated SAP particles and to a method of surface treating SAP particles with a sufficient amount of a hydroxyalkylurea (HAU) to substantially improve the water-absorption and water retention properties of the SAP particles. In particular, the present invention is directed to applying an HAU to

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a surface of the SAP particle, then heating the surface-treated SAP particles at about 90°C to about 170°C for about 60 to about 180 minutes to form surface crosslinks on the SAP particles.

5           In accordance with the present invention, SAP particles possess improved water absorption and water retention properties as a result surface treatment with a hydroxyalkylurea. Treatment with an HAU is especially effective when performed on  
10 polyacrylate salts, hydrolyzed polyacrylamides, or other polymers having a plurality of pendant neutralized carboxyl groups.

          Therefore, the present invention is directed to surface-treated SAP particles having about  
15 0.001 to about 10 parts by weight of an HAU per 100 parts by weight of SAP particles, and applied to the surfaces of the SAP particles to crosslink the molecular chains existing at least in the vicinity of the surface of the SAP particles.

20           One aspect of the present invention is to provide such surface-treated SAP particles, and to a method of manufacturing the surface-treated SAP particles comprising applying a sufficient amount of an HAU to surfaces of the SAP particles and heating  
25 the surface-treated SAP particles at a sufficient temperature for a sufficient time for the HAU to react with pendant groups on a polymer comprising the SAP particle to form surface crosslinks on the SAP particle.

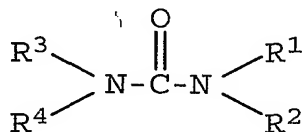
30           Another aspect of the present invention is to heat the surface-treated SAP particles at about 100°C to about 160°C for about 90 to about 150 min-

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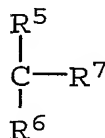
utes to form surface crosslinks on the SAP particles.

Yet another aspect of the present invention is to provide surface-treated SAP particles exhibiting a high retention capacity, high gel strength, and high absorbency under load. This aspect is achieved by surface coating a particle-shaped SAP with about 0.001% to about 10% by weight of an HAU and subsequently heating to about 90°C to about 170°C.

Another aspect of the present invention is to provide an SAP particle having surface crosslinks provided by a hydroxyalkylurea having the structure:

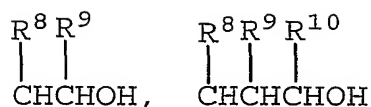


wherein R<sup>1</sup> is



R<sup>2</sup> is H or R<sup>5</sup>, R<sup>3</sup> is H or R<sup>5</sup>, and R<sup>4</sup> is H, R<sup>1</sup>, or R<sup>5</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup>, independently, are H, CH<sub>2</sub>OH,

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or C<sub>1</sub>-C<sub>4</sub>alkyl, R<sup>8</sup>, R<sup>9</sup>, and R<sup>10</sup>, independently, are H, methyl, or ethyl.

10

Still another object of the present invention is to provide SAP particles surface crosslinked with a hydroxyalkylurea in an amount sufficient to substantially improve the water absorbency and water retention properties of the SAP particles, such as retention capacity, absorption rate, and gel strength, and to maintain a "dry feel" for the SAP particles after significant liquid absorption.

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These and other aspects and advantages of the present invention will become apparent from the following detailed description of the preferred embodiments.

20

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

25

In accordance with the present invention, SAP particles are surface treated with a hydroxyalkylurea to substantially increase the rate of liquid absorption, amount of liquid absorption, and overall retention of liquids by the SAP particles. Surface-treatment of the SAP particles at any time after polymerization and sufficient drying to form solid SAP particles improves liquid absorption properties. For economics and ease of manufacture, the surface treatment is most advantageously performed immediately after the SAP particles are synthesized,

30

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dried to an appropriate water content, and sized, such as by grinding.

As will become apparent from the following detailed description of the preferred embodiments, a hydroxyalkylurea surface treatment substantially improves the water absorption properties of SAP particles, which can be either acidic or basic in nature. Of particular utility are SAP particles containing a plurality of pendant, neutralized carboxyl groups along the polymer chain.

As stated above, the surface treatment of SAP particles is well known. However, many surface crosslinking agents exhibit disadvantages. Some surface crosslinking agents have toxic properties and, therefore, cannot be used in the sensitive field of hygiene because they pose a threat to health or the environment. For example, in addition to the risk of skin irritation, epoxy, glycidyl, isocyanate, and organic halogen compounds, have a sensitizing effect, and frequently have a carcinogenic and mutagenic potential. Polyamines are avoided as surface crosslinking agents because of possible nitrosamine formation. In any case, when used in diapers and other sanitary articles, residual amounts of toxicologically critical crosslinking agents must be removed from the SAP particles, which involves additional process steps and increases the cost of the SAP particles.

In addition, a majority of the commonly used surface crosslinking agents required heating at temperatures in excess of 180°C in order to react with the SAP particles and form surface crosslinks. Heating at such a high temperature can increase the

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residual monomer content of the surface crosslinked SAP particles. An increased residual monomer content poses both toxicological and environmental concerns, and is unacceptable commercially.

5           The high temperature required to form surface crosslinks also causes the SAP particles to degrade in color from white or off-white to tan or brown. The tan to brown color of the SAP particles is esthetically unacceptable to consumers, who  
10       equate the tan to brown color of the SAP particles to an inferior product. The combination of color degradation and increased residual monomer can lead to SAP particles that do not meet production specifications and, therefore, refused by the purchaser  
15       and/or consumer. The present invention overcomes these disadvantages associated with prior surface crosslinking agents by utilizing an HAU as the surface crosslinking agent for the SAP particles.

          The identity of the SAP particles utilized  
20       in the present invention is not limited. The SAP particles are prepared by methods well known in the art, for example, solution or emulsion polymerization. The SAP particles, therefore, can comprise an acidic water-absorbing resin, a basic water-absorb-  
25       ing resin, a blend of an acidic and basic water-absorbing resin, or a multicomponent SAP particle as disclosed in WO 99/25393, the disclosure of which is incorporated herein by reference.

          The SAP particles are prepared, for exam-  
30       ple, by:

          (1) copolymerizing an acrylate salt and a crosslinking monomer in aqueous solution, and drying the resulting gel-like hydrous polymer by heating;

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(2) dispersing an aqueous solution of acrylic acid and/or an alkali metal acrylate, a water-soluble radical polymerization initiator, and a crosslinkable monomer in an alicyclic and/or an aliphatic hydrocarbon solvent in the presence of a surface-active agent, and subjecting the mixture to suspension polymerization;

(3) saponifying copolymers of vinyl esters and ethylenically unsaturated carboxylic acids or their derivatives;

(4) polymerizing starch and/or cellulose, a monomer having a carboxyl group or capable of forming a carboxyl group upon hydrolysis, and a crosslinking monomer in an aqueous medium, and, as required, hydrolyzing the resulting polymer; or

(5) reacting an alkaline substance with a maleic anhydride-type copolymer containing maleic anhydride and at least one monomer selected from  $\alpha$ -olefins and vinyl compounds, and, as required, reacting the reaction product with a polyepoxy compound.

Other methods and monomers that provide SAP particles also are known in the art.

Generally, acidic water-absorbing resins have carboxylate, sulfonate, sulfate, and/or phosphate groups incorporated along the polymer chain. Polymers containing these acid moieties are synthesized either from monomers previously substituted with one or more of these acidic functional groups or by incorporating the acidic functional group into the polymer after synthesis. To incorporate carboxyl groups into a polymer, any of a number of ethylenically unsaturated carboxylic acids can be



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homopolymerized or copolymerized. Carboxyl groups also can be incorporated into the polymer chain indirectly by hydrolyzing a homopolymer or copolymer of monomers such as acrylamide, acrylonitrile, methacrylamide, and alkyl acrylates or methacrylates.

An acidic water-absorbing resin present in an SAP particle can be either a strong or a weak acidic water-absorbing resin. The acidic water-absorbing resin can be a single resin, or a mixture of resins. The acidic resin can be a homopolymer or a copolymer.

The acidic water-absorbing resin typically is a neutralized, lightly crosslinked acrylic-type resin, such as neutralized, lightly crosslinked polyacrylic acid. The lightly crosslinked acidic resin typically is prepared by polymerizing an acidic monomer containing an acyl moiety, e.g., acrylic acid, or a moiety capable of providing an acid group, i.e., acrylonitrile, in the presence of a free radical crosslinker, i.e., a polyfunctional organic compound. The acidic resin can contain other copolymerizable units, i.e., other monoethylenically unsaturated comonomers, well known in the art, as long as the polymer is substantially, i.e., at least 10%, and preferably at least 25%, acidic monomer units. To achieve the full advantage of the present invention, the acidic resin contains at least 50%, and more preferably, at least 75%, and up to 100%, acidic monomer units. The acidic resin is neutralized at least 50 mole %, and preferably at least 70 mole %, with a base prior to surface crosslinking.

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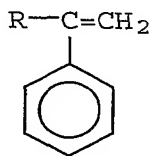
Ethylenically unsaturated carboxylic acid and carboxylic acid anhydride monomers, and salts, useful in the acidic water-absorbing resin include acrylic acid, methacrylic acid, ethacrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -cyanoacrylic acid,  $\beta$ -methylacrylic acid (crotonic acid),  $\alpha$ -phenylacrylic acid,  $\beta$ -acryloxypropionic acid, sorbic acid,  $\alpha$ -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid,  $\beta$ -stearylacrylic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene, 2-methyl-2-butene dicarboxylic acid, maleamic acid, N-phenyl maleamide, maleamide, maleic anhydride, fumaric anhydride, itaconic anhydride, citraconic anhydride, mesaconic anhydride, methyl itaconic anhydride, ethyl maleic anhydride, diethylmaleate, methylmaleate, and maleic anhydride.

Sulfonate-containing acidic resins can be prepared from monomers containing functional groups hydrolyzable to the sulfonic acid form, for example, alkenyl sulfonic acid compounds and sulfoalkylacrylate compounds. Ethylenically unsaturated sulfonic acid monomers include aliphatic or aromatic vinyl sulfonic acids, such as vinylsulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, acrylic and methacrylic sulfonic acids, such as sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, 2-vinyl-4-ethylbenzene, 2-allylbenzene sulfonic acid, 1-phenylethylene sulfonic acid, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid, and 2-acrylamide-2-methylpropane sulfonic acid.

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Sulfate-containing acidic resins are prepared by reacting homopolymers or copolymers containing hydroxyl groups or residual ethylenic unsaturation with sulfuric acid or sulfur trioxide. Examples of such treated polymers include sulfated polyvinylalcohol, sulfated hydroxyethyl acrylate, and sulfated hydroxypropyl methacrylate. Phosphate-containing acidic resins are prepared by homopolymerizing or copolymerizing ethylenically unsaturated monomers containing a phosphoric acid moiety, such as methacryloxy ethyl phosphate.

Copolymerizable monomers for introduction into the acidic resin, or into the basic resin, include, but are not limited to, ethylene, propylene, isobutylene, C<sub>1</sub> to C<sub>4</sub> alkyl acrylates and methacrylates, vinyl acetate, methyl vinyl ether, and styrenic compounds having the formula:



wherein R represents hydrogen or a C<sub>1-6</sub> alkyl group, and wherein the phenyl ring optionally is substituted with one to four C<sub>1-4</sub> alkyl or hydroxy groups.

Suitable C<sub>1</sub> to C<sub>4</sub> alkyl acrylates include, but are not limited to, methyl acrylate, ethyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate, and the like, and mixtures thereof. Suitable C<sub>1</sub> to C<sub>4</sub> alkyl methacrylates include, but are not limited to, methyl methacrylate, ethyl

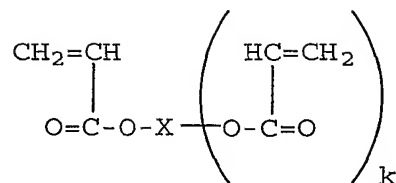
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methacrylate, isopropyl methacrylate, n-propyl-methylmethacrylate, n-butyl methacrylate, and the like, and mixtures thereof or with C<sub>1-4</sub> alkyl acrylates. Suitable styrenic compounds include, but  
5 are not limited to, styrene,  $\alpha$ -methylstyrene, p-methylstyrene, t-butyl styrene, and the like, and mixtures thereof or with C<sub>1-4</sub> alkyl acrylates and/or methacrylates.

As set forth above, polymerization of  
10 acidic monomers, and optional copolymerizable monomers, most commonly is performed by free radical processes in the presence of a polyfunctional organic compound. The acidic resins are crosslinked to a sufficient extent such that the polymer is  
15 water insoluble. Crosslinking renders the acidic resins substantially water insoluble, and, in part, serves to determine the absorption capacity of the resins. For use in absorption applications, an acidic resin is lightly crosslinked, i.e., has a  
20 crosslinking density of less than about 20%, preferably less than about 10%, and most preferably about 0.01% to about 7%.

A crosslinking agent most preferably is used in an amount of less than about 7 wt%, and  
25 typically about 0.1 wt% to about 5 wt%, based on the total weight of monomers. Examples of crosslinking polyvinyl monomers include, but are not limited to, polyacrylic (or polymethacrylic) acid esters represented by the following formula (I); and bisacryl-  
30 amides, represented by the following formula (II).

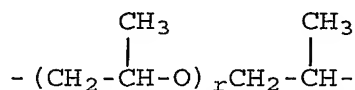
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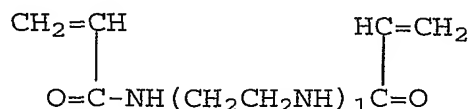
wherein X is ethylene, propylene, trimethylene,  
cyclohexyl, hexamethylene, 2-hydroxypropylene,  
10  $-(\text{CH}_2\text{CH}_2\text{O})_p\text{CH}_2\text{CH}_2-$ , or



15

p and r are each an integer 5 to 40, and k is 1 or  
2;

20



25

wherein 1 is 2 or 3.

The compounds of formula (I) are prepared  
by reacting polyols, such as ethylene glycol, pro-  
pylene glycol, trimethylolpropane, 1,6-hexanediol,  
glycerin, pentaerythritol, polyethylene glycol, or  
30 polypropylene glycol, with acrylic acid or meth-  
acrylic acid. The compounds of formula (II) are  
obtained by reacting polyalkylene polyamines, such

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as diethylenetriamine and triethylenetetramine, with acrylic acid.

Specific crosslinking monomers include, but are not limited to, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, ethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, dipentaerythritol pentaacrylate, pentaerythritol tetraacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate, tris(2-hydroxyethyl)isocyanurate trimethacrylate, divinyl esters of a polycarboxylic acid, diallyl esters of a polycarboxylic acid, triallyl terephthalate, diallyl maleate, diallyl fumarate, hexamethylenebismaleimide, trivinyl trimellitate, divinyl adipate, diallyl succinate, a divinyl ether of ethylene glycol, cyclopentadiene diacrylate, tetraallyl ammonium halides, or mixtures thereof. Compounds such as divinylbenzene and divinyl ether also can be used as crosslinking agents. Especially preferred crosslinking agents are N,N'-methylenebisacrylamide, N,N'-methylenebismethacrylamide,

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ethylene glycol dimethacrylate, and trimethylolpropane triacrylate.

The acidic resin, either strongly acidic or weakly acidic, can be any resin that acts as an SAP in its neutralized form. Examples of acidic resins include, but are not limited to, polyacrylic acid, hydrolyzed starch-acrylonitrile graft copolymers, starch-acrylic acid graft copolymers, saponified vinyl acetate-acrylic ester copolymers, hydrolyzed acrylonitrile copolymers, hydrolyzed acrylamide copolymers, ethylene-maleic anhydride copolymers, isobutylene-maleic anhydride copolymers, poly(vinylsulfonic acid), poly(vinylphosphonic acid), poly(vinylphosphoric acid), poly(vinylsulfuric acid), sulfonated polystyrene, poly(aspartic acid), poly(lactic acid), and mixtures thereof. The preferred acidic resins are the polyacrylic acids.

The final acidic SAP particle contains from about 50 to 100 percent neutralized pendant carboxylate salt units. Accordingly, it may be necessary to neutralize carboxylic acid groups. Neutralization of carboxylic acid groups is accomplished using a strong organic or inorganic base, such as sodium hydroxide, potassium hydroxide, ammonia, ammonium hydroxide, or an organic amine.

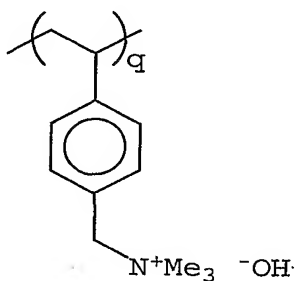
The sequence and the number of reactions (e.g., polymerization, hydrolysis, and neutralization) performed to obtain the desired acid functionality attached to acidic resin backbone are not critical. Any number and sequence resulting in a final SAP particle which possesses 0 to about 90 percent copolymerizable monomer units and about 10 to about 100 percent monomer units having pendant

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acid groups, and neutralized at least 50 mole %, is suitable.

Analogous to the acidic resin, a basic water-absorbing resin present in the SAP particles can be a strong or weak basic water-absorbing resins. The basic water-absorbing resin can be a single resin or a mixture of resins. The basic resin can be a homopolymer or a copolymer. The identity of the basic resin is not limited as long as the basic resin is capable of reacting with an HAU or a 2-oxazolidone. The strong basic resins typically are present in the hydroxide (OH) or bicarbonate (HCO<sub>3</sub>) form.

The basic water-absorbing resin typically is a lightly crosslinked acrylic-type resin, such as a poly(vinylamine). The basic resin also can be a polymer such as a lightly crosslinked polyethylenimine, a poly(allylamine), a poly(allylguanidine), a poly(dimethyldiallylammonium hydroxide), a quaternized polystyrene derivative, such as

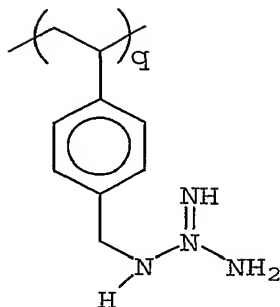


a guanidine-modified polystyrene, such as



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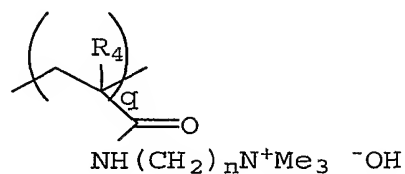
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a quaternized poly((meth)acrylamide) or ester analog, such as

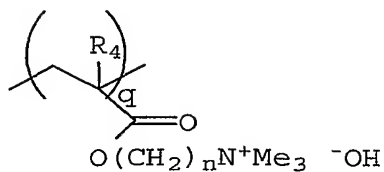
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or

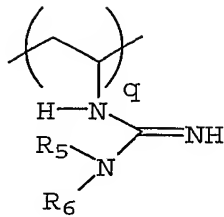
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wherein Me is methyl,  $R_4$  is hydrogen or methyl,  $n$  is a number 1 to 8, and  $q$  is a number from 10 to about 100,000, or a poly(vinylguanidine), i.e., poly(VG), a strong basic water-absorbing resin having the general structural formula (III)

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(III)

wherein q is a number from 10 to about 100,000, and R<sub>5</sub> and R<sub>6</sub>, independently, are selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>3</sub>-C<sub>6</sub> cycloalkyl, benzyl, phenyl, alkyl-substituted phenyl, naphthyl, and similar aliphatic and aromatic groups. The lightly crosslinked basic water-absorbing resin can contain other copolymerizable units and is cross-linked using a polyfunctional organic compound, as set forth above with respect to the acidic water-absorbing resin.

A basic water-absorbing resin used in the present SAP particles typically contains an amino or a guanidine group. Accordingly, a water-soluble basic resin can be crosslinked in solution by suspending or dissolving an uncrosslinked basic resin in an aqueous or alcoholic medium, then adding a di- or polyfunctional compound capable of crosslinking the basic resin by reaction with the amino groups of the basic resin. Such crosslinking agents include, for example, multifunctional aldehydes (e.g., glutaraldehyde), multifunctional acrylates (e.g., butanediol diacrylate, TMPTA), halohydrins (e.g., epichlorohydrin), dihalides (e.g., dibromopropane), disulfonate esters (e.g.,  $ZS(O_2)O-(CH_2)_n-OF(O)_2Z$ , wherein n is 1 to 10, and Z is methyl or tosyl),

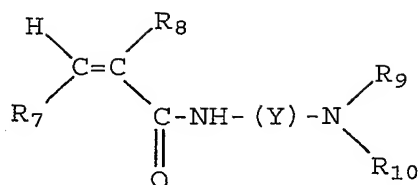
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multifunctional epoxies (e.g., ethylene glycol diglycidyl ether), multifunctional esters (e.g., dimethyl adipate), multifunctional acid halides (e.g., oxalyl chloride), multifunctional carboxylic acids (e.g., succinic acid), carboxylic acid anhydrides (e.g., succinic anhydride), organic titanates (e.g., TYZOR AA from DuPont), melamine resins (e.g., CYMEL 301, CYMEL 303, CYMEL 370, and CYMEL 373 from Cytec Industries, Wayne, NJ), hydroxymethyl ureas (e.g., N,N'-dihydroxymethyl-4,5-dihydroxyethylene-urea), and multifunctional isocyanates (e.g., toluene diisocyanate or methylene diisocyanate). Cross-linking agents for basic resins also are disclosed in Pinschmidt, Jr. et al. U.S. Patent No. 5,085,787, incorporated herein by reference, and in EP 450 923.

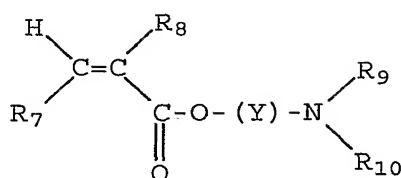
Conventionally, the crosslinking agent is water or alcohol soluble, and possesses sufficient reactivity with the basic resin such that crosslinking occurs in a controlled fashion, preferably at a temperature of about 25°C to about 150°C. Preferred crosslinking agents are ethylene glycol diglycidyl ether (EGDGE), a water-soluble diglycidyl ether, and a dibromoalkane, an alcohol-soluble compound.

The basic resin, either strongly or weakly basic, therefore, can be any resin that acts as an SAP in its charged form. Examples of basic resins include a poly(vinylamine), a polyethylenimine, a poly(vinylguanidine), a poly(allylamine), a poly(allylguanidine), or a poly(dialkylaminoalkyl (meth)acrylamide) prepared by polymerizing and lightly crosslinking a monomer having the structure

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or its ester analog



wherein  $\text{R}_7$  and  $\text{R}_8$ , independently, are selected from the group consisting of hydrogen and methyl, Y is a divalent straight chain or branched organic radical having 1 to 8 carbon atoms,  $\text{R}_9$  is hydrogen, and  $\text{R}_{10}$  is hydrogen or an alkyl radical having 1 to 4 carbon atoms. Preferred basic resins include a poly(vinyl-amine), polyethylenimine, poly(vinylguanadine), poly(methylaminoethyl acrylamide), and poly(methyl-aminopropyl methacrylamide).

There is no particular restriction on the shape of the SAP particles used in this invention. The SAP particles can be in the form of spheres obtained by inverse phase suspension polymerization, flakes obtained by drum drying, or irregularly shaped particles obtained by pulverizing solid polymer. From the standpoint of the speed of absorption, the SAP particles preferably are small, and

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typically the particle size is about 20 to about 2000  $\mu\text{m}$ , preferably about 50 about 850  $\mu\text{m}$ .

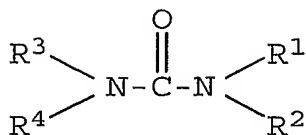
The SAP particles, comprising an acidic resin, basic resin, a blend of acidic and basic resin, or multicomponent SAP particles, are surface treated by applying a surface crosslinking agent to the surface of the SAP particles, followed by heating the particles. Surface treatment results in surface crosslinking of the SAP particles. It has been found that surface treating SAP particles with an HAU enhances the ability of the SAP particles to absorb and retain aqueous media under a load.

In general, surface crosslinking is achieved by contacting SAP particles with a solution of an HAU to wet predominantly only the outer surfaces of the SAP particles. Surface crosslinking of the SAP particles then is performed, preferably by heating at least the wetted surfaces of the SAP particles.

The surface crosslinking agent utilized in the present invention is an HAU or a 2-oxazolidone. For example, HAUs are disclosed in Lee et al. U.S. Patent No. 5,840,822, and Kielbania, Jr. et al. U.S. Patent No. 5,858,549, each incorporated herein by reference. HAUs also are disclosed in Peterson U.S. Patent No. 3,635,835, Hoy et al. U.S. Patent No. 5,039,759, and Haas et al. U.S. Patent No. 4,546,121.

An HAU useful in the present invention has the following formula:

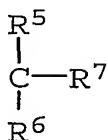
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wherein R<sup>1</sup> is

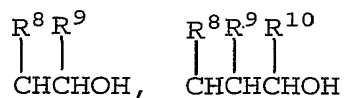
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R<sup>2</sup> is H or R<sup>5</sup>, R<sup>3</sup> is H or R<sup>5</sup>, and R<sup>4</sup> is H, R<sup>1</sup>, or R<sup>5</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup>, independently, are H, CH<sub>2</sub>OH,

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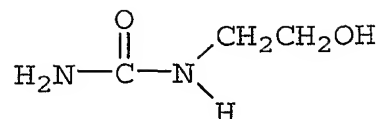
or C<sub>1</sub>-C<sub>4</sub>alkyl, R<sup>8</sup>, R<sup>9</sup>, and R<sup>10</sup>, independently, are H, methyl, or ethyl. The HAUs useful in the present invention have a single urea group (i.e., NC(=O)N) and at least one hydroxyl group. In preferred em-

bodiments, at least two carbon atoms are disposed between the urea group and each of the hydroxyl groups.

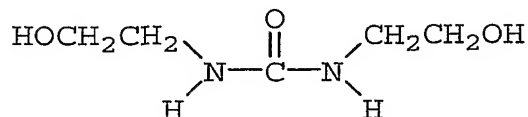
Most preferred HAUs have the formula:

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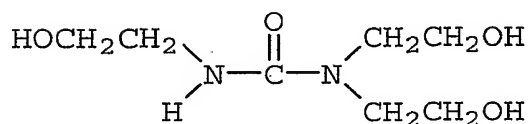
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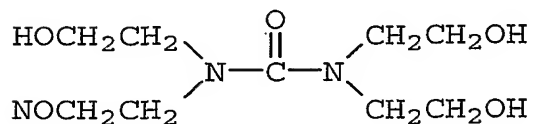


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and



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Specific examples of HAU compounds include, but are not limited to, N,N-bis(2-hydroxyethyl)urea, tetrakis(2-hydroxyethyl)urea, tris(2-hydroxyethyl)urea, N,N'-bis(2-hydroxyethyl)urea, N,N'-bis(3-hydroxypropyl)urea, N,N'-bis(4-hydroxybutyl)urea, 2-urea-2-ethyl-1,3-propanediol, (2-hydroxyethyl)urea, (3-hydroxypropyl)urea, (4-hydroxybutyl)urea, 1,1-dimethyl-2-hydroxyethylurea, 1-ethyl-2-hydroxyethylurea, (2-hydroxyethyl)ethyleneurea, N,N'-bishydroxymethylurea, N,N-bishydroxymethylurea, N-(2-hydroxyethyl)-N,N'-ethyleneurea, N-

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(2-hydroxyethyl)-N'-butylurea, N,N-bis(2-hydroxyethyl)-N'-butylurea, N-(2-hydroxy-1-propyl)-N'-butylurea, N,N'-bis(3-hydroxy-2,2-dimethyl-1-propyl)urea, N,N'-bis(2-hydroxyethyl)-N,N'-ethy-  
5 eneurea, N-(2-hydroxyethyl)-N'-methylurea, N,N'-bis(2-hydroxyethyl)-N-ethylurea, N,N,N'-tris(2-hydroxyethyl)-N'-methylurea, N,N'-bis(2-hydroxyethyl)-N,N'-diethylurea, N,N'-bis(2-hydroxyethyl)-N,N'-dimethylurea, N-(2-hydroxypropyl)urea, N-(2-hydroxyethyl)-  
10 N'-(3-hydroxypropyl)urea, N-(2-hydroxypropyl)-N'-(2-hydroxyethyl)urea, N,N'-bis(2-hydroxyethyl)-N'-(2-hydroxypropyl)urea, N,N-bis(2-hydroxyethyl)-N'-(3-hydroxypropyl)urea, N,N-bis(3-hydroxypropyl)-N'-(3-hydroxypropyl)urea, tetrakis(3-hydroxypropyl)urea,  
15 N,N-bis(3-hydroxypropyl)-N'-(2-hydroxyethyl)urea, N,N-bis(3-hydroxypropyl)-N'-(2-hydroxypropyl)urea, tris(2-hydroxypropyl)urea, N,N-bis(2-hydroxypropyl)-N'-(3-hydroxypropyl)urea, N,N-bis(2-hydroxypropyl)-N'-(2-hydroxyethyl)urea, N,N-bis(2-hydroxyethyl)-N-  
20 (3-hydroxybutyl)urea, N-(1,1-bis(hydroxymethylene)-ethylurea, N-(1,1-bis(hydroxymethylene)-2-hydroxy)-ethylurea, and mixtures thereof.

The HAUs useful in the present invention are prepared by reaction sequences well known in the  
25 art. For example, the preparation of HAUs is disclosed in U.S. Patent Nos. 5,858,549; 5,840,822; 5,039,759; 3,635,835; and 4,546,121, each incorporated herein by reference, wherein urea, potassium cyanate, or dimethylcarbonate is reacted with an  
30 amine, in sufficient molar quantities to provide a monohydroxy or polyhydroxy alkylurea. Examples of amines used in the reaction include, but are not limited to, ethanolamine, diethanolamine, 3-amino-1-



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propanol, 2-amino-2-ethyl-1,3-propanediol, 4-amino-butanol, 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, aminoethylethanolamine, 2-aminopropanol, diisopropylamine, 4-amino-2-butanol, 2-amino-2-hydroxymethyl-1,3-propanediol, and mixtures thereof.

In particular, an HAU is prepared by admixing one mole of urea with one to two molar equivalents of an amine. The reaction mixture is heated to 115°C, and the reaction mixture is held at 115°C for eight hours under a nitrogen blanket. Ammonia is evolved during the reaction. When the reaction is complete, the resulting HAU can be used without further purification.

The following table illustrates various nonlimiting amine used in a reaction with urea, and molar ratios, to provide an HAU:

Amine	g Amine	g Urea	Time (hr.)	Temp (°C)
ethanolamine	40.7	20.00	8	115
diethanolamine	35.0	20.00	8	115
ethanolamine	30.5	30.00	8	115
diethanolamine	50.0	14.29	8	115
2-(methylamino)ethanol	37.5	30.00	8	115
2-(methylamino)ethanol	50.0	20.00	8	115

Typically, the SAP particles are surface treated using a solution of an HAU. The solution contains about 0.01% to about 4%, by weight, HAU, and preferably about 0.4% to about 2%, by weight, HAU, in a suitable solvent, for example, water, an alcohol, or a glycol. The solution can be applied

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as a fine spray onto the surface of freely tumbling SAP particles at a ratio of about 1:0.01 to about 1:0.5 parts by weight SAP particles to solution of HAU.

5                   To achieve the desired absorption properties, the HAU is distributed evenly on the surfaces of the SAP particles. For this purpose, mixing is performed in suitable mixers, e.g., fluidized bed mixers, paddle mixers, a rotating disc mixer, a  
10 ribbon mixer, a screw mixer, milling rolls, or twin-worm mixers.

                  The amount of HAU used to surface treat the SAP particles varies depending upon the identity of SAP particles. Generally, the amount of HAU used  
15 to surface treat the SAP particles is about 0.001 to about 10 parts by weight per 100 parts by weight of the SAP particles. When the amount of HAU exceeds 10 parts by weight, the SAP particles are too highly surface crosslinked, and the resulting SAP particles  
20 have a reduced absorption capacity. On the other hand, when SAP particles are surface crosslinked with less than 0.001 part by weight HAU, there is no observable effect.

                  A preferred amount of HAU used to surface  
25 crosslink the SAP particles is about 0.01 to about 5 parts by weight per 100 parts, by weight, SAP particles. To achieve the full advantage of the present invention, the amount of HAU used as a surface crosslinking agent is about 0.05 to about 1 part, by  
30 weight, per 100 weight parts of SAP particles.

                  The drying and surface crosslinking of the surface-treated SAP particles are achieved by heating the surface-treated particles at a suitable

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temperature, e.g., about 90°C to about 170°C, and preferably about 100°C to about 165°C. To achieve the full advantage of the present invention, the surface-treated particles are heated at about 100°C to about 160°C. At this temperature, the SAP particles are surface crosslinked with the HAU without degrading the color of the SAP particles and without increasing the residual monomer content of the SAP particles.

The surface-treated SAP particles are heated for about 60 to about 180 minutes, preferably about 60 to about 150 minutes, to effect surface crosslinking. To achieve the full advantage of the present invention, the SAP particles are heated for about 75 to about 120 minutes.

Ordinary dryers or heating ovens can be used for heating the surface-treated SAP particles and the HAU. Such heating apparatus includes, for example, an agitated trough dryer, a rotating dryer, a rotating disc dryer, a kneading dryer, a fluidized bed dryer, a pneumatic conveying dryer, and an infrared dryer. However, any other method of reacting the HAU with the polymer of the SAP particle to achieve surface crosslinking of the SAP particles, such as microwave energy, can be used. In the surface treating and surface crosslinking steps, the mixer can be used to perform simultaneous mixing and heating of the HAU and SAP particles, if the mixer is of a type that can be heated.

As previously stated, surface treating with an HAU, and subsequent or simultaneous heating, provides additional polymer crosslinks in the vicinity of the surface of the SAP particles. The grada-

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tion in crosslinking from the surface of the SAP particles to interior, i.e., the anisotropy of crosslink density, can vary, both in depth and profile. Thus, for example, the depth of surface crosslinking can be shallow, with a relatively sharp transition from a high level to a low level of crosslinking. Alternatively, for example, the depth of surface crosslinking can be a significant fraction of the dimensions of the SAP particle, with a broader transition.

Depending on size, shape, porosity, as well as functional considerations, the degree and gradient of surface crosslinking can vary within a given type of SAP particle. Depending on variations in surface:volume ratio within the SAP particles (e.g., between small and large particles), it is typical for the overall level of crosslinking to vary over the group of SAP particles (e.g., is greater for smaller particles).

Surface crosslinking generally is performed after the final boundaries of the SAP particles are essentially established (e.g., by grinding, extruding, or foaming). However, it is also possible to effect surface crosslinking concurrently with the creation of final boundaries. Furthermore, some additional changes in SAP particle boundaries can occur even after surface crosslinks are introduced.

The following examples illustrate the present surface crosslinked SAP particles. It should be understood, however, that these examples are merely illustrative, and that the scope of this invention is not limited to these examples.

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In the following examples, the SAP particles are lightly crosslinked polyacrylic acid polymers, neutralized about 75% to about 80% with sodium hydroxide. The sodium polyacrylate was made by methods well known in the art.

#### Examples 1-9

A 5%, by weight, solution of the HAU in propylene glycol (25% by weight) and water (70% by weight) was applied to the surface of the SAP particles, to provide surface crosslinking in an amount of 2000 ppm HAU (based on the weight of the SAP particles). The surface-treated SAP particles then were heat treated at about 165°C for about 90 minutes. The performance results are summarized in Table 1.

#### Examples 10-18

A 4%, by weight, solution of the HAU in propylene glycol (25% by weight) and water (71% by weight) was applied to the surface of SAP particles, to provide surface crosslinking in an amount of 1600 ppm HAU (based on the weight of the SAP particles). The surface-treated SAP particles then were heat treated at about 165°C for about 90 minutes. The performance results are summarized in Table 1.

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Table 1				
Example <sup>1)</sup>	CR	CRC	AUL (0.70 psi)	SFC
1	0.04	26.7	23.4	28.1
2	0.04	26.8	23.9	26.8
3	0.04	26.6	23.4	17.5
4	0.04	26.8	23.7	26.5
5	0.04	26.6	23.3	27.6
6	0.04	26.7	22.9	20.5
7	0.04	26.6	23.8	27.7
8	0.04	27.3	23.5	21.8
9	0.04	26.3	23.6	23.0
10	0.04	26.6	23.9	29.2
11	0.04	26.8	24.5	45.8
12	0.04	26.6	24.4	30.5
13	0.04	26.6	24.1	26.1
14	0.04	26.2	23.6	32.8
15	0.04	27.2	23.9	29.8
16	0.04	26.7	23.9	27.9
17	0.04	26.9	23.8	29.9
18	0.04	26.3	24.2	26.8

<sup>1)</sup> Examples 1, 4, 10, 13--N,N-bis(2-hydroxyethyl)urea,  
 Examples 2, 3, 11, 12--N,N'-bis(2-hydroxyethyl)urea,  
 Examples 5 and 14--N-(2-hydroxyethyl)urea,  
 Examples 6 and 15--tetrakis(2-hydroxyethyl)urea,  
 Examples 7 and 16--N-methyl-N-(2-hydroxyethyl)urea,  
 Examples 8 and 17--N,N'-dimethyl-N,N'-bis(2-hydroxyethyl)  
 urea, and  
 Examples 9 and 18--NACRYLINK M, a monohydroxyalkylurea  
 available from National Starch and Chemical Corp.,  
 Wilmington, DE.

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In the test results set forth in Table 1, the surface-treated SAP particles were tested for absorption under load at 0.7 psi (AUL (0.7 psi)). Absorption under load (AUL) is a measure of the ability of an SAP to absorb fluid under an applied pressure, expressed in grams of fluid per gram of SAP. The AUL was determined by the following method as disclosed in U.S. Patent No. 5,149,335, incorporated herein by reference.

An SAP (0.160 g +/-0.001 g) is carefully scattered onto a 140-micron, water-permeable mesh attached to the base of a hollow Plexiglas cylinder with an internal diameter of 25mm. The sample is covered with a 100 g cover plate and the cylinder assembly weighed. This gives an applied pressure of 20 g/cm<sup>2</sup> (0.28 psi). Alternatively, the sample can be covered with a 250 g cover plate to give an applied pressure of 51 g/cm<sup>2</sup> (0.7 psi). The screened base of the cylinder is placed in a 100mm petri dish containing 25 milliliters of a test solution (usually 0.9% saline), and the polymer is allowed to absorb for 1 hour (or 3 hours). By reweighing the cylinder assembly, the AUL (at a given pressure) is calculated by dividing the weight of liquid absorbed by the dry weight of polymer before liquid contact.

The test results in Table 1 also set forth the centrifuge retention capacity (CRC) of the test samples. The centrifuge retention capacity of an SAP is a measure of the absorptive capacity of the SAP. In particular, the CRC test is a method of determining the absorbent capacity of an SAP in grams of 0.9% saline (NaCl) solution per gram of polymer. This test includes swelling the SAP in a

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"teabag" immersed in 0.9% NaCl solution for 30 minutes, then centrifuged for three minutes. The ratio of retained liquid weight to initial weight of the dry SAP is the absorptive capacity of the superabsorbent polymer, or the CRC.

The CRC test was performed as follows:

#### APPARATUS

Electronic Balance, accuracy of 0.0001 gram  
Plastic Tray, 44 cm X 39 cm X 10 cm  
Heat sealer, T-bar plastic model  
Teabag material (CH DEXTER), cut and sealed to produce a teabag 6.25 x 8.5 cm  
Weigh paper or plastic weighing boat  
Timer  
Centrifuge capable of 1400 rpm, 230 mm diameter  
Tongs

#### MATERIALS

SAP test sample  
0.9% NaCl solution prepared with distilled or deionized water

#### SAMPLE PREPARATION

(10 samples per set maximum  
20 samples per 2000 ml NaCl solution)



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- a) Pour approximately 2000 ml of NaCl solution into the tray. The liquid filling height should be approximately 1/2 inch.
- 5 b) Fold teabag paper and seal two sides with heat sealer, leaving one side open for polymer addition. Samples may be run in duplicate (optional).
- 10 c) Weight 0.2000 +/- 0.0050 grams polymer onto weigh paper or plastic weighing boat. Record weight and number.
- 15 d) Mark teabag with corresponding sample number. Transfer polymer to teabag and close open end with heat sealer.
- e) Seal an empty teabag and mark it "blank."
- 20 f) Set the timer for 30 minutes. Hold each teabag horizontally and distribute the polymer evenly throughout the bag. Lay filled teabags and the blank on the surface of the NaCl solution. Submerge each teabag using a spatula to allow
- 25 complete wetting. Start the timer.

Filled teabags were handled carefully with tongs, contacting only the edge of the teabag and not the area filled with polymer.

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- 40 -

**CENTRIFUGE**

- 5 a) After 20 minutes soak time, remove filled teabags and blank from NaCl solution. Position the teabags in the centrifuge with each bag sticking to the outer wall of the centrifuge basket.
- 10 b) Close the centrifuge lid. Set the timer for 3 minutes. Start the centrifuge (ramp up quickly to 1400 rpm) and the timer at the same time. After 3 minutes, turn off the centrifuge (and apply the brake if necessary).
- 15 c) Weigh each filled teabag and blanks. Record weights.

**CALCULATION**

20 CFC (g/g) =

$$\frac{\text{final weight of teabag} - \text{final weight of blank} - \text{dry polymer weight}}{\text{dry polymer weight}}$$

25 The test results in Table 1 further set forth the Saline Flow Conductivity (SFC) of the test samples. The SFC of an SAP is a measure of the permeability of SAP particles when swollen with a liquid to form a hydrogel zone or layer. SFC measures the ability of an SAP to transport saline fluids, such as the ability of the hydrogel layer

30 formed from the swollen SAP to transport body fluids. A material having relatively high SFC value is

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an air-laid web of woodpulp fibers. Typically, an air-laid web of pulp fibers (e.g., having a density of 0.15 g/cc) exhibits an SFC value of about  $200 \times 10^{-7} \text{ cm}^3\text{sec/g}$ . In contrast, typical hydrogel-forming SAPs exhibit SFC values of  $1 \times 10^{-7} \text{ cm}^3\text{sec/g}$  or less. When an SAP is present at high concentrations in an absorbent structure, and then swells to form a hydrogel under usage pressures, the boundaries of the hydrogel come into contact, and interstitial voids in the high SAP concentration region become generally bounded by hydrogel. When this occurs, the permeability or saline flow conductivity properties in this region is generally indicative of the permeability or saline flow conductivity properties of a hydrogel zone formed from the SAP alone. Increasing the permeability of these swollen high concentration regions can provide superior fluid handling properties for the absorbent structure, thus decreasing incidents of leakage, especially at high fluid loadings. A method of determining the SFC value of SAP particles is set forth in Goldman et al. U.S. Patent No. 5,599,335, incorporated herein by reference.

The data in Table 1 show that surface crosslinking using an HAU provides surface-treated SAP particles having an excellent AUL. In addition, an HAU surface crosslinker increased the AUL, without adversely affecting the CRC, which is both beneficial and unexpected in the art. The surface-crosslinked SAP particles of the present invention also have an excellent SFC value, which indicates an ability of the resultant hydrogel to absorb and retain body fluids under normal usage conditions.

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Preferred SAP particles of the present invention are surface crosslinked with an HAU, and have a 0.7 AUL of at least 15, and more preferably at least 20. The preferred surface crosslinked SAP particles typically have a 0.7 AUL of about 15 to about 30. Preferred SAP particles of the present invention also have a CRC of less than 32.4, and more preferably less than 31.5. Preferred SAP particles typically have a CRC of less than 32.4 to about 25. Preferred SAP particles of the present invention have an SFC value of at least about  $15 \times 10^{-7}$  cm<sup>3</sup>sec/g, and preferably at least about  $20 \times 10^{-7}$  cm<sup>3</sup>sec/g. To achieve the full advantage of the present invention, the SFC value of the present surface-crosslinked SAP particles is at least about  $25 \times 10^{-7}$  cm<sup>3</sup>sec/g, and can range to greater than  $60 \times 10^{-7}$  cm<sup>3</sup>sec/g.

Examples 1-16 illustrate that the scope of HAUs useful in surface crosslinking SAP particles is broad. The properties exhibited by the HAU surface-crosslinked SAP particles illustrate that an HAU can be substituted for currently used surface-crosslinking agents, like EGDGE, and overcome disadvantages associated with such crosslinking agents, e.g., color degradation.

Examples 1-16 also show that additional surface crosslinking agents (e.g., a diol) that can be used in combination with the HAU. Cosolvents also can be used in the surface crosslinking of SAP particles using an HAU. Examples of cosolvents include, but are not limited to, alcohols, e.g., methanol, ethanol, and isopropanol, and ketones, e.g., acetone.

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An additional surface crosslinking agent can be any compound that reacts with a pendant moiety of the polymer comprising the SAP particles, and that inhibits the swell of SAP particles, can be used in conjunction with the HAU. Examples of additional surface crosslinking agents include, but are not limited to, diols, triols, polyols, e.g., ethylene glycol, propylene glycol, and 1,3-butanediol, and similar hydroxyl-containing compounds. Divalent and trivalent metal salts can be used as additional surface crosslinking agents, and as swell suppressants. The HAU also can be used in combination with other surface crosslinking agents, such as EGDGE, and especially with any other surface crosslinking compound that can react with the polymer comprising the SAP particles at temperatures below 160°C.

The surface crosslinked SAP particles of the present invention can be used as an absorbent in disposable diapers, sanitary napkins, and similar articles, and can be used in other applications, for example, a dew formation inhibitor for building materials, a water-holding agent for agriculture and horticulture, and a drying agent.

Surface-crosslinked SAP particles of the present invention have advantages over conventional absorbent particles. The surface-crosslinked SAP particles of the invention can be produced at a low cost by a simple method which involves mixing SAP particles with the HAU and heating. The resulting surface-crosslinked SAP particles are less susceptible to fish eye formation than conventional absorbent resins and, therefore, exhibit a high rate of

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liquid absorption. The present surface-crosslinked SAP particles also are white to off-white in color.

Obviously, many modifications and variations of the invention as hereinbefore set forth can be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated by the appended claims.

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WHAT IS CLAIMED IS:

1. Superabsorbent polymer particles comprising 100 parts by weight of a water-absorbing resin and about 0.001 to about 10 parts by weight of a hydroxyalkylurea, wherein the hydroxyalkylurea is present at surfaces of the water-absorbing resin and crosslinks polymer chains at the surfaces of the water-absorbing resin.

2. The particles of claim 1 wherein the particles contain about 0.01 to about 4 parts by weight of the hydroxyalkylurea agent per 100 parts by weight of the water-absorbing resin.

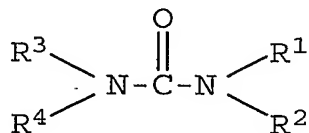
3. The particles of claim 1 wherein the particles contain about 0.4 to about 2 parts by weight of the hydroxyalkylurea per 100 parts by weight of the water-absorbing resin.

4. The particles of claim 1 wherein the hydroxyalkylurea has at least two carbon atoms disposed between the urea group and each hydroxyl group.

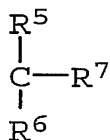
5. The particles of claim 4 wherein the hydroxyalkylurea has two carbon atoms disposed between the urea group and each hydroxyl group.

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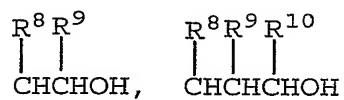
6. The particles of claim 1 wherein the hydroxyalkylurea has the structure



wherein R<sup>1</sup> is



R<sup>2</sup> is H or R<sup>5</sup>, R<sup>3</sup> is H or R<sup>5</sup>, and R<sup>4</sup> is H, R<sup>1</sup>, or R<sup>5</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup>, independently, are H, CH<sub>2</sub>OH,

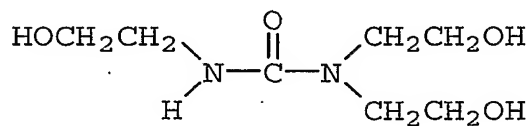
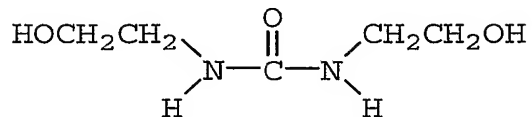
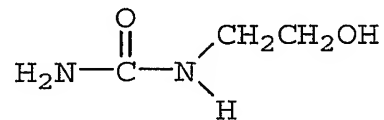


or C<sub>1</sub>-C<sub>4</sub>alkyl, and R<sup>8</sup>, R<sup>9</sup>, and R<sup>10</sup>, independently, are H, methyl, or ethyl.

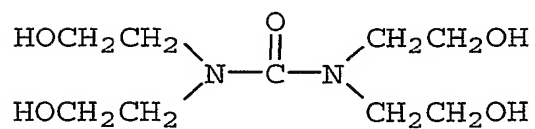


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7. The particles of claim 1 wherein the hydroxyalkylurea has the structure



, or



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8. The particles of claim 1 wherein the hydroxyalkylurea is selected from the group consisting of N,N-bis(2-hydroxyethyl)urea, tetrakis(2-hydroxyethyl)urea, tris(2-hydroxyethyl)urea, N,N'-bis(2-hydroxyethyl)urea, N,N'-bis(3-hydroxypropyl)urea, N,N'-bis(4-hydroxybutyl)urea, 2-urea-2-ethyl-1,3-propanediol, (2-hydroxyethyl)urea, (3-hydroxypropyl)urea, (4-hydroxybutyl)urea, 1,1-dimethyl-2-hydroxyethylurea, 1-ethyl-2-hydroxyethylurea, (2-hydroxyethyl)ethyleneurea, N,N'-bishydroxymethylurea, N,N-bishydroxymethylurea, N-(2-hydroxyethyl)-N,N'-ethyleneurea, N-(2-hydroxyethyl)-N'-butylurea, N,N-bis(2-hydroxyethyl)-N'-butylurea, N-(2-hydroxy-1-propyl)-N'-butylurea, N,N'-bis(3-hydroxyl-2,2-dimethyl-1-propyl)urea, N,N'-bis(2-hydroxyethyl)-N,N'-ethyleneurea, N-(2-hydroxyethyl)-N'-methylurea, N,N'-bis(2-hydroxyethyl)-N-ethylurea, N,N,N'-tris(2-hydroxyethyl)-N'-methylurea, N,N'-bis(2-hydroxyethyl)-N,N'-diethylurea, N,N'-bis(2-hydroxyethyl)-N,N'-dimethylurea, N-(2-hydroxypropyl)urea, N-(2-hydroxyethyl)-N'-(3-hydroxypropyl)urea, N-(2-hydroxypropyl)-N'-(2-hydroxyethyl)urea, N,N'-bis(2-hydroxyethyl)-N'-(2-hydroxypropyl)urea, N,N-bis(2-hydroxyethyl)-N'-(3-hydroxypropyl)urea, N,N-bis(3-hydroxypropyl)-N'-(3-hydroxypropyl)urea, tetrakis(3-hydroxypropyl)urea, N,N-bis(3-hydroxypropyl)-N'-(2-hydroxyethyl)urea, N,N-bis(3-hydroxypropyl)-N'-(2-hydroxypropyl)urea, tris(2-hydroxypropyl)urea, N,N-bis(2-hydroxypropyl)-N'-(3-hydroxypropyl)urea, N,N-bis(2-hydroxypropyl)-N'-(2-hydroxyethyl)urea, N,N-bis(2-hydroxyethyl)-N-(3-hydroxybutyl)urea, N-(1,1-bis(hydroxymethylene)ethylurea, N-(1,1-bis(hydroxy-

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methylene)-2-hydroxy)ethylurea, and mixtures thereof.

9. The particles of claim 1 wherein the water-absorbing resin comprises an acidic water-absorbing resin.

10. The particles of claim 9 wherein the acidic water-absorbing resin is a neutralized, lightly crosslinked acrylic-type resin containing at least 10% acidic monomer units.

11. The particles of claim 10 wherein the acidic monomer units have a carboxylate, sulfonate, sulfate, or phosphate group.

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12. The particles of claim 9 wherein the acidic monomer units are selected from the group consisting of acidic water-absorbing resin include acrylic acid, methacrylic acid, ethacrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -cyanoacrylic acid,  $\beta$ -methylacrylic acid,  $\alpha$ -phenylacrylic acid,  $\beta$ -acryloxypropionic acid, sorbic acid,  $\alpha$ -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid,  $\beta$ -stearylacrylic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene, 2-methyl-2-butene dicarboxylic acid, maleamic acid, N-phenyl maleamide, maleamide, maleic anhydride, fumaric anhydride, itaconic anhydride, citraconic anhydride, mesaconic anhydride, methyl itaconic anhydride, ethyl maleic anhydride, diethylmaleate, methylmaleate, maleic anhydride, vinylsulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, an acrylic sulfonic acid, a methacrylic sulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, 2-vinyl-4-ethylbenzene, 2-allylbenzene sulfonic acid, 1-phenylethylene sulfonic acid, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid, 2-acrylamide-2-methylpropane sulfonic acid, sulfated polyvinylalcohol, sulfated hydroxyethyl acrylate, sulfated hydroxypropyl methacrylate, methacryloxyethyl phosphate, and mixtures thereof.

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13. The particles of claim 9 wherein the acidic water-absorbing resin is selected from the group consisting of a starch-acrylic acid graft copolymers, a saponified vinyl acetate-acrylic ester copolymer, a hydrolyzed acrylonitrile copolymer, a hydrolyzed acrylamide copolymer, an ethylene-maleic anhydride copolymer, an isobutylene-maleic anhydride copolymer, poly(vinylsulfonic acid), poly(vinylphosphonic acid), poly(vinylphosphoric acid), poly(vinylsulfuric acid), sulfonated polystyrene, poly(aspartic acid), poly(lactic acid), and mixtures thereof, neutralized 20 to 100 mole percent with a base.

14. The particles of claim 1 wherein the water-absorbing resin is polyacrylic acid neutralized 50 to 100 mole percent.

15. The particles of claim 1 wherein the water-absorbing resin comprises a basic water-absorbing resin.

16. The particles of claim 15 wherein the basic water-absorbing resin is a neutralized, lightly crosslinked resin containing at least 10% basic monomer units.

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17. The particles of claim 15 wherein the basic water-absorbing resin is selected from the group consisting of a poly(vinylamine), a poly-(alkylaminoalkyl (meth)acrylamide, a polyethylenimine, a poly(allylamine), a poly(allylguanidine), a poly(dimethylallylammonium hydroxide), a quaternized polystyrene, a guanidine-modified polystyrene, a quaternized poly(meth)acrylamide or ester analog thereof, a poly(vinylguanidine), and mixtures thereof.

18. The particles of claim 1 wherein the water-absorbing resin comprises a mixture of an acidic water-absorbing resin and a basic water-absorbing resin.

19. The particles of claim 1 wherein the water-absorbing resin comprises multicomponent superabsorbent polymer particles.

20. The particles of claim 1 having an absorption under a load of 0.7 psi after one hour of at least 20 grams of 0.9% saline per gram of particles.

21. The particles of claim 1 having an AUL at 0.7 psi of greater than 15 and a CRC of less than 32.4.

22. The particles of claim 23 having an AUL at 0.7 psi of greater than 20.

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23. The particles of claim 22 having a CRC of less than 31.5.

24. The particles of claim 23 having a saline flow conductivity of at least  $20 \times 10^{-7}$  cm<sup>3</sup>sec/g.

25. Surface crosslinked superabsorbent polymer particles obtained by mixing 100 parts, by weight, of a superabsorbent polymer with about 0.001 to about 10 parts, by weight, of a hydroxyalkylurea to form surface-treated superabsorbent polymer particles, then heating the surface-treated superabsorbent particles at about 90°C to about 170°C for about 60 to about 180 minutes to form surface crosslinks on the surface-treated superabsorbent polymer particles.

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26. A method of preparing surface cross-linked superabsorbent polymer particles comprising:

- (a) providing 100 parts by weight of superabsorbent polymer particles;
- (b) forming a solution comprising about 0.5% to about 50% by weight of a hydroxyalkylurea in a solvent capable of solubilizing the surface cross-linking agent;
- (c) applying the solution of (b) to surfaces of (a) to provide surface-treated superabsorbent polymer particles having about 0.001 to about 10 parts, by weight, of the hydroxyalkylurea per 100 parts, by weight, of superabsorbent polymer particles in the vicinity of the surfaces of the superabsorbent polymer particles; and
- (d) heating the surface-treated superabsorbent polymer particles at about 90°C to about 170°C for about 60 to about 180 minutes to form surface crosslinks in the vicinity of the surface of the superabsorbent polymer particles.

27. The method of claim 26 wherein step (c) is performed prior to step (d).

28. The method of claim 26 wherein steps (c) and (d) are performed simultaneously.



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29. The method of claim 28 wherein the surface crosslinking agent solution of step (b) further comprises a second surface crosslinking agent selected from the group consisting of a diol, a triol, a polyol, a divalent metal, a trivalent metal, a diglycidyl ether, a diamine, a halohydrin, a polyisocyanate, a dihaloalkane, a polyfunctional aziridine compound, a dialdehyde, a disulfonate ester, a diester, a multifunctional acid halide, an organic titanate, a melamine resin, a hydroxymethyl urea, and mixtures thereof.

30. The method of claim 29 wherein the second surface crosslinking agent comprises ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, ethylene glycol diglycidyl ether, and mixtures thereof.

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31. The method of claim 26 wherein the surface crosslinking agent solution of step (b) further comprises a second surface crosslinking agent capable of forming surface crosslinks on the superabsorbent polymer particles at a temperature of about 90°C to about 160°C.

32. A method of preparing surface cross-linked superabsorbent polymer particles comprising:

(a) polymerizing a mixture containing (i) unsaturated polymerizable monomers having acid groups or basic groups, and (ii) a polyfunctional crosslinking agent, dissolved in (iii) a solvent comprising water to form a superabsorbent polymer hydrogel;

(b) adding a sufficient amount of a hydroxyalkylurea to the superabsorbent polymer hydrogel to provide about 0.001 to about 10 parts, by weight, of the surface crosslinking agent per 100 parts, by weight, of the superabsorbent polymer; and

(c) heating the product of step (b) at about 90°C to about 170°C to dry the superabsorbent polymer hydrogel, form superabsorbent polymer particles, and form crosslinks on the surface of the superabsorbent polymer particles.

33. Surface crosslinked superabsorbent polymers prepared by the method of claim 32.